



Investigation on Ilmenite Placer Ore as a Precursor for Synthetic Rutile

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Abstract

Faced with diminished reserves of natural rutile, synthetic rutile has become an important source of titanium used in paint and paper pigments. The study explores the influence of temperature (50, 75 and 100 °C), pulp density (5, 15 and 25 wt.-%), stirring speed (360 and 530 rpm) and process conditions (oxidative and reductive leaching) on the purification of synthetic rutile from a Malaysian ilmenite placer deposit. The study is aimed at determining the best combination of parameters that will produce a product of 95.5% synthetic rutile. A number of processes exist to obtain synthetic rutile from ilmenite ores. These are sulphate, alkaline and chloride based. However, the HCl treatment route was chosen for this study. This process exhibits fast kinetics, excellent impurities removal and the potential to regenerate the acid makes it sustainable and environmentally friendly. Samples of the ore screened to a 106 – 212 µm size fraction were treated with 700 mL of 18% (5.5 M) HCl. Leaching was conducted in 1 L reactor vessels with one suited for atmospheric pressure and the other for high-pressure operations for a duration of 4 hours each. It was concluded that temperature was the main parameter influencing the level of purification for the synthetic rutile obtained. The pulp density was found to influence the amount of titanium and iron released in the leachate solution. However the objective of purifying the ilmenite ore to 95.5% synthetic rutile was not achieved. The highest purity achieved was 77 % with the process conditions of 100 °C, 15 wt.-% and 360 rpm.

SEM analysis showed that the temperature and pulp density were intrinsically linked to the formation of a product layer around the ilmenite grains during the HCl treatment. Despite being effectively observed through SEM, this and other available data could not be conclusively used to validate a suitable kinetic model for the HCl treatment. The data did however show that the HCl purification of the synthetic rutile occurred in two phases. In the first phase, governed by chemical reactions, the acid permeates the particles facilitated by porosity and fractures of the grain and dissolves both iron and titanium. When a certain amount of titanium accumulates in the leachate solution it precipitates and forms a layer around the grains. From this point on, a second phase begins in which kinetics are



now governed by diffusion of iron through this layer which prevents any further penetration of acid into the grains.

1 Introduction

Titanium is the ninth most abundant element and constitutes 0.6 % of the earth's crust. It is mainly used in one of two forms. As sponge metal for aerospace applications, armour plating, marine and medical applications (Bedinger 2014; Zhang et al., 2011). This accounts for 5 % of industrially produced titanium. The other 95 % is produced in the form of titanium dioxide, a white pigment used in paint, plastics, paper but also in cosmetics, porcelain, ceramics, nanoparticles and photo-electrochemical materials. The minerals ilmenite (FeTiO_3) and rutile (TiO_2) are the main sources of titanium. But with diminishing resources of natural rutile considerable attention has been turned towards obtaining it, especially in the form of titanium dioxide, from ilmenite rich ores. In this form it is termed synthetic rutile.

Typically, ilmenite ore is crushed and milled then concentrated using magnetic separation prior to leaching. Additionally, pre-treatment such as oxidative and or reductive roasting may be conducted to make the ilmenite ores more susceptible to leaching. The leaching is conducted in order to purify the concentrate by dissolving impurities, mostly Fe, and leaving behind titanium dioxide. A number of processes, chloride, sulphate and ammonia based, exist to purify ilmenite ores to obtain synthetic rutile. However, this study focuses on HCl leaching directly on ilmenite material which follows the chemistry described by the equations below:



The leaching of the impurities is governed by parameters such as particle size, temperature, stirring speed, pulp density, acid concentration, presence of a reducing agent, pressure and leaching duration. Each parameter can be changed to increase the purity of the synthetic rutile or diminish the quantity of remaining iron, taking into account acid and energy consumption.

Based on literature (Jackson and Wadsworth, 1976) the particle size fraction chosen for this study (106 – 212 μm) at the selected temperature range (50 – 100 °C) will not influence the rate or extent of leaching. Sasikumar et al. (2007) showed that temperatures in excess of 80 °C significantly increase the amount of Fe leached and at the same time engender titanium polymerisation. The latter causes the synthetic rutile to precipitate preventing it from dissolving in solution. An increase in stirring speed from 300 to 500 rpm increases Fe extraction from 75 to 90 % and a further increase up to 700 rpm, drives it from 90 to 92 % (Gireesh et al., 2015). Typically speeds over 700 rpm are not used in industry. It must also be noted that the resulting particle size must be observed as increasing stirring speed can also generate attrition. The optimally reduced particle size is an important factor for white



pigment production. The best synthetic rutile input for chlorination should have grains of approximately 150 μm . Higher solid to liquid ratios in excess of 10 wt.-% diminish the titanium content in solution and so increase the rutile recovery (Sasikumar et al., 2007).

Hydrochloric and sulfuric acid are mainly used for industrial ilmenite leaching because they are less dangerous and more widely applied than fluorhydric and nitric acid. HCl is highly corrosive – this is one of its main drawbacks – but is more effective than sulfuric acid. The traditional sulfate process produces lower quality products for most applications and large quantities of waste iron sulfate. Therefore, the production cost is generally higher for sulphate processes than for chlorine ones. Indeed, the polymerization point does not exist for sulphate leaching. The synthetic rutile production requires then more steps, which increases the production costs (Sasikumar et al., 2007). A high acid concentration better dissolves iron and titanium due to the increased quantity of acid content for removal of ions in ilmenite (Gireesh et al., 2015). Acid concentration does not influence the precipitation point of titanium (if pH stays < 0.5 M). Even if a higher acid concentration removes more iron it also increases titanium losses in the solution after precipitation (Sasikumar et al., 2007). Reducing agents such as CaCl_2 , MgCl_2 , NaCl and Fe powder are known to improve the efficiency of the leaching process. However this would interfere with the downstream process of HCl regeneration hence they will not be used in this study. Although the most common practice is to leach at atmospheric pressure, Chen (1974) observed that an increase in pressure resulted in an increase in synthetic rutile recovery. Finally, a retention time of 4 hrs has been reported as the most optimal one (Sasikumar et al., 2007).

The aim of the study is however to focus on the following parameters: temperature (resulting from pressure), pulp density and stirring speed. An added objective is to understand the mechanism of the leaching process

2 Characterization of the Concentrate

The ore used was a placer deposit ore obtained from Malaysia. It has been crushed and milled to micron size and concentrated via magnetic separation prior to being received for the study. The chemical composition obtained by XRF can be seen in Table 1 and mineralogical information obtained via XRD is detailed in Table 2.

Table 1: Chemical composition by quantitative XRF of the concentrate (97.2 %)

| TiO_2 | Fe_2O_3 | MnO | SiO_2 | MgO | Al_2O_3 | CaO | P_2O_5 |
|----------------|-------------------------|------|----------------|------|-------------------------|------|------------------------|
| 56.23 | 39.67 | 1.90 | 1.03 | 0.64 | 0.67 | 0.10 | 0.07 |

Table 2: Mineralogy of the concentrate as per XRD analysis (100 %)

| Ilmenite (FeTiO_3) | Rutile (TiO_2) | Hematite (Fe_2O_3) | Magnetite (Fe_3O_4) |
|-------------------------------|---------------------------|--------------------------------------|---------------------------------------|
| 72 | 22 | 4 | 2 |

3 Experimental Programme (Equipment and Methods)

Appropriate sample sizes for test work were prepared using a two-way riffle and quartering. Prior to leaching tests, the samples were subjected to magnetic separation to remove as much of the magnetite as possible using a Jeffrey-Taylor JT103 magnetic separator. The next step was to screen them to a size fraction of 106 – 212 μm using vibrating screens. Leaching with HCl was conducted with one of the two vessels shown in Figure 1.

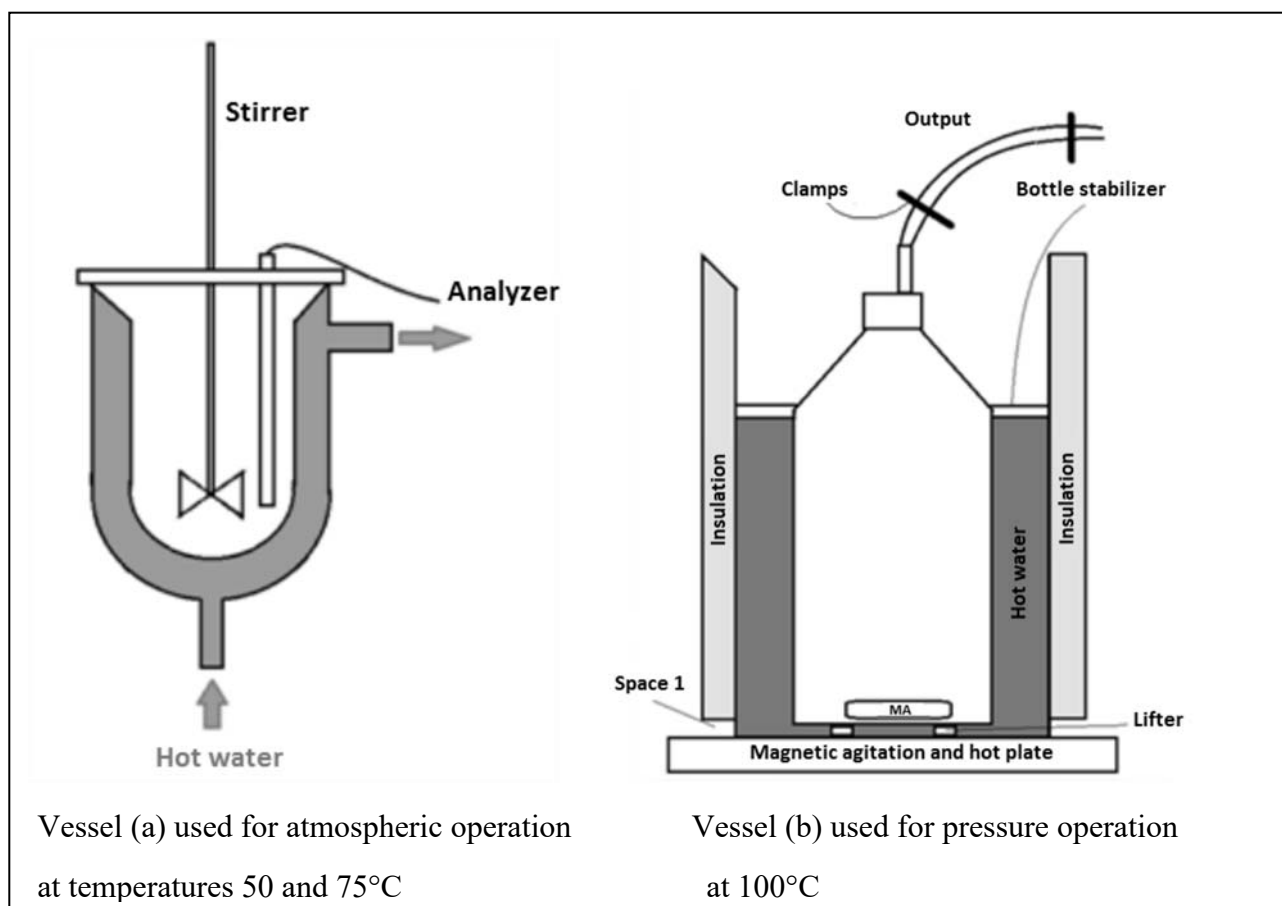


Figure 1: Vessels (a) and (b) used for atmospheric and pressure leaching

Vessel (a) was used for atmospheric leaching conducted at temperatures 50 and 75 °C. It was an open glass vessel closed by a Teflon plate with two holes. One hole was for the agitator which had a boring rod made of Teflon. The second was used to insert tubing with a syringe attached to the end for sampling (indicated as “Analyzer” in the diagram). The vessel was plunged in a thermostatic bath in order to maintain temperature.

Vessel (b) was used to conduct pressure leaching at 100 °C. Pressure was not controlled but was the result of the vaporisation of the acid in the tightly sealed reactor. At 100 °C it was estimated that the overpressure was around 0.8 bar. The reactor was a 1 L glass one capable of withstanding up to 1.5 bar overpressure. The reactor was placed in a water-bath insulated all around with rockwool and heated using a hot plate/magnetic agitator. The reactor was elevated so that the particles at the bottom



would not be cooked and to achieve a uniform temperature distribution inside. The pulp was agitated using a magnetic bar. Sampling was conducted by removing the hose inside the reactor to get the sample by tilting the bottle. During this procedure, two clamps were required. The first one was opened and the bottle was tilted allowing the pregnant leach solution to flow into the external hose to the second clamp. The first clamp was then closed and the reactor was straightened in the hot bath. The second clamp was then opened and the sample was collected. The reactor was outside from the bath only during 15 seconds thus allowing the solution in the reactor to maintain its temperature.

In both cases, 700 mL of 18 % HCl solution was used to leach the samples at the selected pulp densities with changes being made with the sample volumes. The slurry was heated up to the desired temperature and leached for a duration of 4 hrs from that point. Samples of solution were taken at intervals of 15 min, 30 min, 1 hr, 1.5 hrs, 2.5 hrs, 3.5 hrs and 4 hrs for analysis of Ti and Fe by ICP-AES. On completion of the test the pulp was filtered using a filter paper (Whatman grade 3), a Buchner funnel and bench-top vacuum pump. The filter cake was then washed to remove iron chloride and then dried. Sub-samples were taken for analysis via XRD to determine the rutile purity. The full range of tests to investigate the influence of the process parameters can be seen in Table 3.

In addition to the tests shown in Table 3, leaching tests were conducted with duration of 1 hr and 4 hrs to understand the leaching mechanism. The samples from the filter cakes were mounted onto non-conductive resin to fabricate polished sections and analysed using SEM. An XL30 ESEM-FEG with Bruker 120 eV environmental scanning electron microscope was used to this end. This analysis has enabled to observe the topography of the grains and follow the porosity evolution during the leaching via BSE (backscattered electrons).

Table 3: Leaching tests summary

| No | Temperature (°C) | Pulp Density (wt.-%) | Stirring Speed (rpm) | Pressure |
|----|------------------|----------------------|----------------------|----------|
| 1 | 50 | 15 | 360 | Atm |
| 2 | 75 | 5 | 360 | Atm |
| 3 | 75 | 15 | 360 | Atm |
| 4 | 75 | 15 | 530 | Atm |
| 5 | 75 | 25 | 360 | Atm |
| 6 | 75 | 15 | 360 | Atm |
| 7 | 100 | 15 | 360 | Pressure |



4 Results and Discussion

4.1 Temperature Effect

As one can see in Figure 2 (a), an increase in temperature significantly increases iron dissolved in the leaching liquor. The leaching does not last long enough to be able to say that the plateau is reached after 3.5 hours of leaching. This assumption would require more data at the end of the curve. Moreover, if we look at the titanium content in Figure 2 (b), it is easy to see that titanium does not reach a plateau. In fact, titanium content is decreasing at 75 °C and at 100 °C and is increasing at 50 °C.

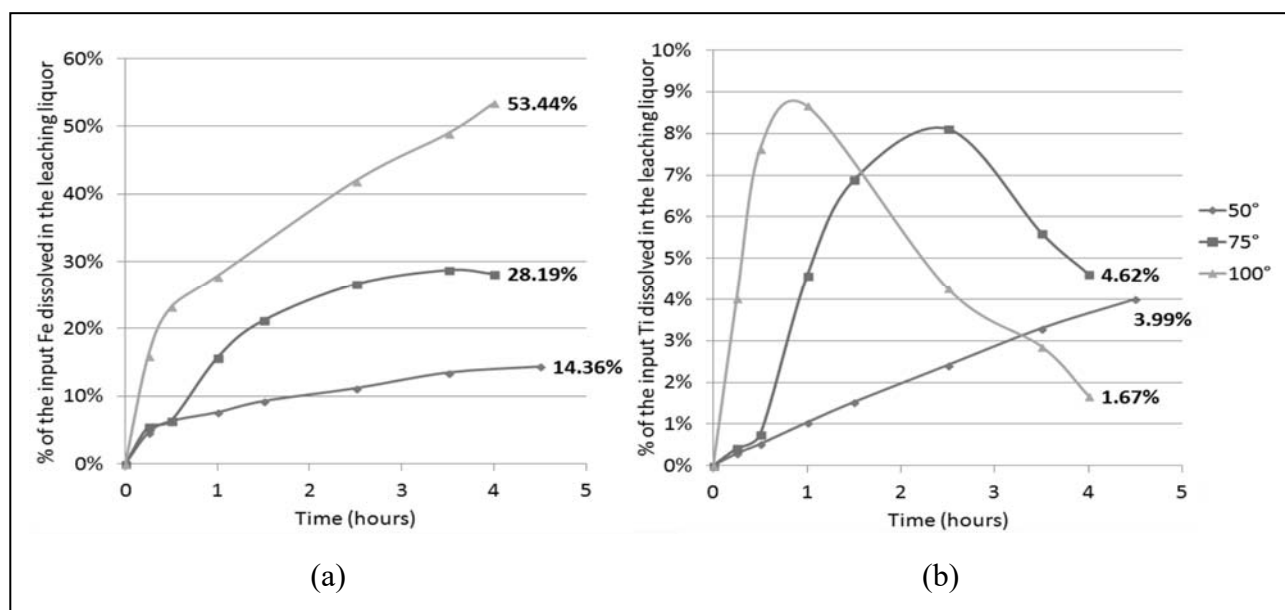


Figure 2: Effect of the temperature (50 °C, 75 °C, 100 °C) on the iron and titanium dissolution with 5.5M HCl, 15 wt.-% of pulp density with a stirring speed of 360 rpm and under atmospheric pressure for an experiment at 50 °C and in closed reactor for the others.

Titanium is precipitating as expected, but this phenomenon was observed only at the 75 °C and 100 °C. Indeed, the required titanium content to have precipitation has not been reached yet. Consequently, the temperature influences the precipitation moment (2.5 h at 75 °C and about 45 min at 100 °C). As the temperature increases the reaction speed, the concentration in $[Ti^{4+}]$ increases faster when the temperature is higher and consequently, the precipitation occurs sooner. The graphics represent the percentage of iron and titanium coming from the feed dissolved in the acid. This is why the maxima are different. Indeed, given that the solution is diluted when the pulp density is lower, the percentage of titanium dissolved must be higher to reach the precipitation point. Moreover, a higher temperature lead to less titanium remaining at the end of the leaching and as a consequence increases the leaching efficiency. However, in practice, the quantity dissolved at the maximum remains the same according to the temperatures but changes according to the reactor: 9 g/L in the open reactor and 6.5 g/l in the closed one. Hence the maximum titanium content (in g/L) in the PLS only depends on the oxidizing or reducing conditions in the reactor.



4.2 Pulp Density Effect

Generally, according to the literature, a decrease in the pulp density improves the dissolution rate. However, in our case, only iron has to be dissolved and not titanium given that the aim is to recover TiO_2 in the cake (Figure 3 (a)). Consequently, a compromise between iron removal and titanium losses has to be found.

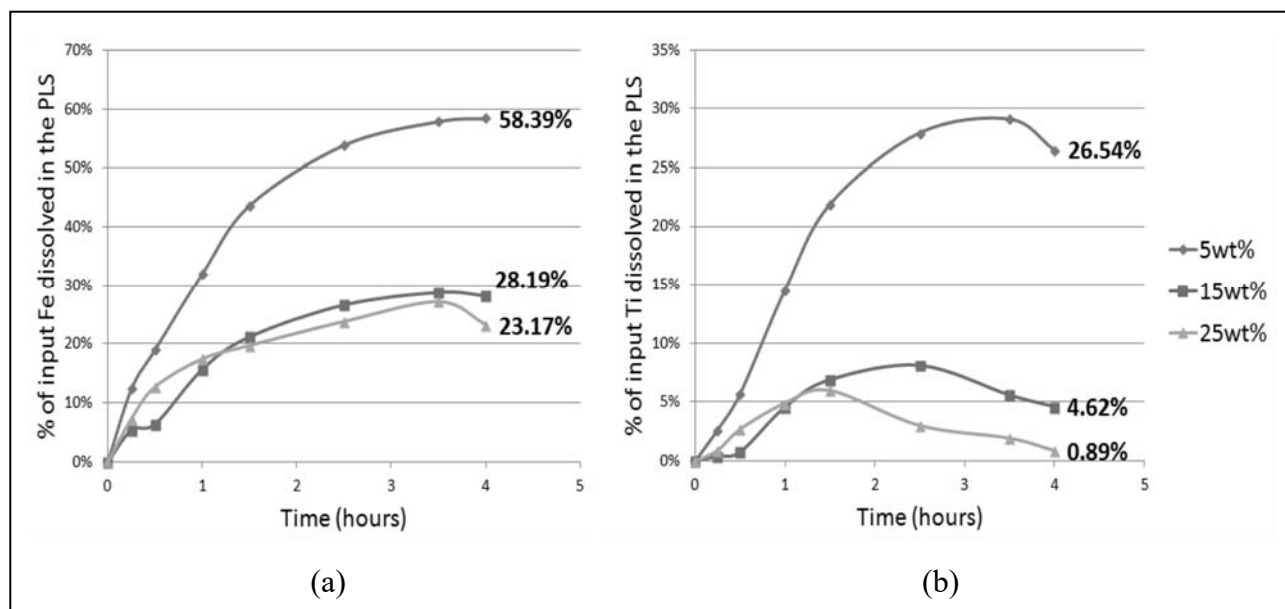


Figure 3: Effect of the pulp density (5 wt.-%, 15 wt.-%, 25 wt.-%) on iron and titanium dissolution with 5.5 M HCl, at 75 °C, with a stirring speed of 360 rpm and at atmospheric pressure.

As for the temperature, the precipitation point is also influenced by the pulp density. Indeed, the more material we have, the faster the required titanium content in the PLS is reached. If we look at the 5 wt.-% pulp density, we notice that the precipitation point comes later in the process (Figure 3 (b)). As a consequence, we could extend the leaching duration to recover the iron. However, iron content in the PLS seems to reach a plateau. So, a prolonged leaching would not decrease the iron content.

Even if the iron dissolution is worse at 25 wt.-% pulp density, the synthetic rutile yield is increased (Figure 3 (a)). These results are not due to the removal of the iron from ilmenite but due to less losses in titanium that forms TiO_2 . A way to increase the iron dissolution would be to increase the acid content. Indeed, for 15 wt.-% of pulp density, the solution is supersaturated in HCl. Moreover, the pH does not change during the leaching or its changes are negligible. However, for 25 wt.-% of pulp density, the ratio between ilmenite and hydrochloric acid is about 1.54. However, given the acid regeneration, this difference is lower and the ratio is closer to 2. To compensate this decrease in ilmenite/HCl ratio, 8.5 M HCl can be used.



4.3 Stirring Speed Effect

Theoretically, a higher stirring speed should increase the contact between the particles and consequently should increase the reaction rate. However, at 75 °C, as shown in Figure 4 (a) and (b), the dissolution remains the same until the precipitation point of Ti is reached (Figure (b)). Then, a higher stirring speed has a negative effect by removing less iron and dissolving more titanium. However, the balance of iron for the leaching at 75 °C and 360 rpm is lower (88 %). Hence this assumption was checked at 50 °C. At this temperature, the overall reaction is only governed by chemical reactional steps and not by diffusion within 5.5 hours. At 50 °C, a high stirring speed decreases the solubility. As a consequence, we can conclude that high stirring speed can provoke dead zones because the solution is stuck against the walls of the reactor, which decreases the reaction rate. However, when the temperature is increased, this effect becomes negligible until the precipitation point is reached. Another reactor that creates more turbulences could be used in order to verify this assumption. In fact, we cannot conclude whether increasing the stirring speed is more efficient or not. We can only conclude that with a cylindrical-type reactor, the difference in efficiency could be due to insufficient turbulence.

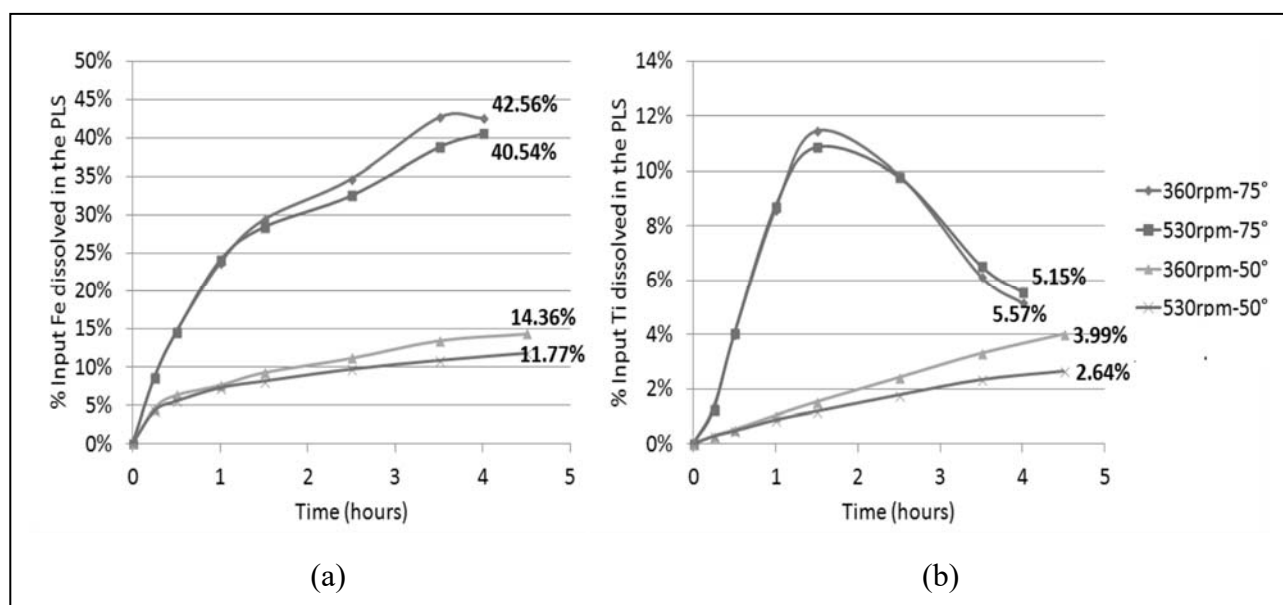


Figure 4: Effect of the Stirring Speed (360 rpm and 530 rpm) on the iron and titanium dissolution with 5.5 M HCl, at 75 °C, with 15 % of pulp density.

The deviations seen in the graphs in Fig. 4 could be due to an analytical error. Indeed, the metal balance does not reach 100 %. In fact, XRD on the cake confirms this assumption: by keeping a stirring speed of 360 rpm and a temperature of 75 °C, a synthetic rutile content of 37 wt.-% is obtained in opposition to 30 wt.-% for a stirring speed of 530 rpm. At 50 °C, a high stirring speed dissolves less titanium and consequently, the synthetic rutile content in the cake is greater (31 wt.-% for 530 rpm instead of 27 wt.-% for 360 rpm). Hence a lower stirring speed seems better for the chosen reactor system.



4.4 Interaction between Temperature, Stirring Speed and Pulp Density

Figure 5 (a) shows that a low pulp density improves iron dissolution and has a greater impact than the temperature on it. However, a low pulp density engenders titanium losses (Figure 5 (b)). A way to avoid losses and to dissolve as much iron as possible is to decrease the pulp density and increase the temperature at the same time. Nevertheless, even if high temperature lowers the leaching time by displacing the precipitation point to the left, a low pulp density provokes larger titanium concentration before precipitation. As a result, this non-negligible content of titanium takes time to precipitate, thus increasing the leaching time.

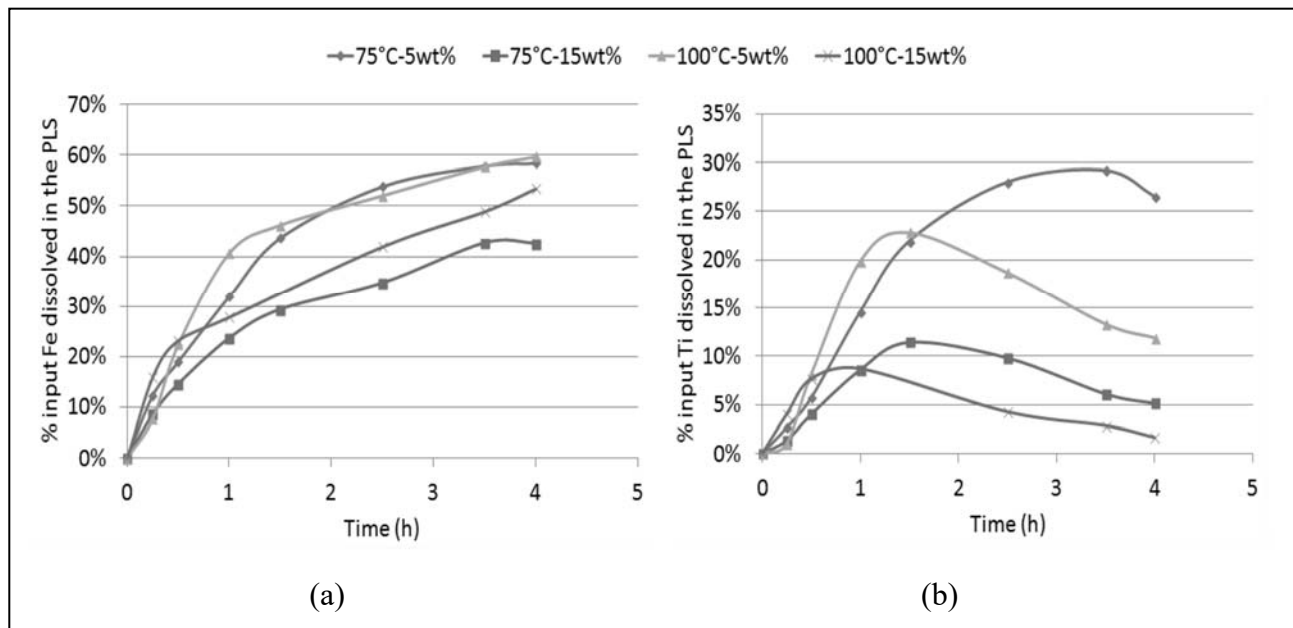


Figure 5: Interaction between temperature and pulp density with time and at 360 rpm stirring speed.

Figure 6 (a) shows that the temperature mainly influences the synthetic rutile grade in the cake even if it has a non-negligible influence on iron and titanium dissolution degree. Pulp density is for its part the main parameter that influences iron and titanium content in the leaching liquor (Figure 6 (b)).

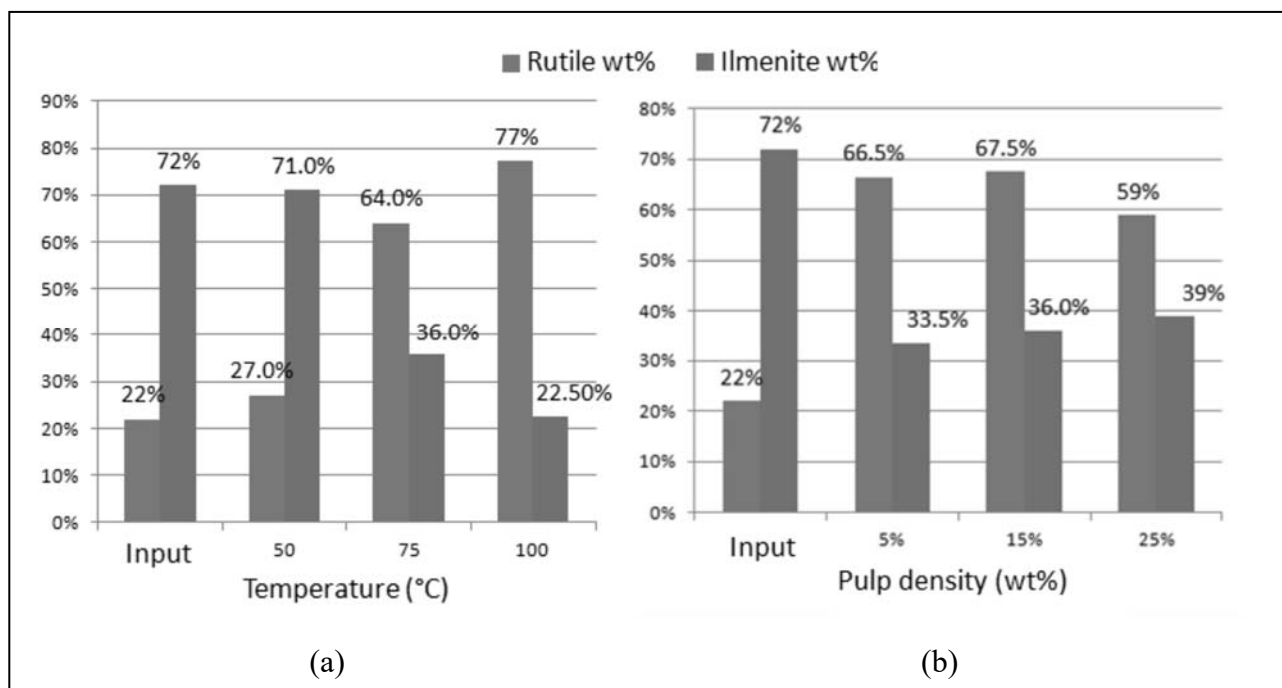


Figure 6: Effect from of temperature and pulp density on synthetic rutile grade in the cake.

4.5 Mechanism of Leaching

The grains micrographs pictured in Figure 7 suggest that after 1 hour the acid penetrates inside the mineral through fractures and porosity. Consequently, when the mineral is less porous, only the external layer is attacked, dissolving one part and transforming the other part of ilmenite grains into rutile. The leaching seems to follow a classical chemical equilibrium pattern, titanium and mainly iron present in the mineral are dissolved without forming a layer around the grains (Figure 7 (b)). This can also be seen in Figure 8 (a) and (b), when a greater proportion of titanium is seen after 4 hour leaching with remaining iron inside the core of the particles. During the leaching, hydrochloric acid attacks the grains through the pores but also along the external layer. Consequently, the porosity increases the leaching efficiency. Before the precipitation point, it can be seen that hematite is dissolved firstly followed by ilmenite. When the precipitation moment is reached, a small layer mainly composed of titanium is formed. This layer protects the grains that keep their shape and size. The leaching enters then in the second phase. During this phase, the reaction is not governed by chemical reaction but by diffusion of iron through this layer. Thus, the remaining iron is then generally located around the centre of the grains.

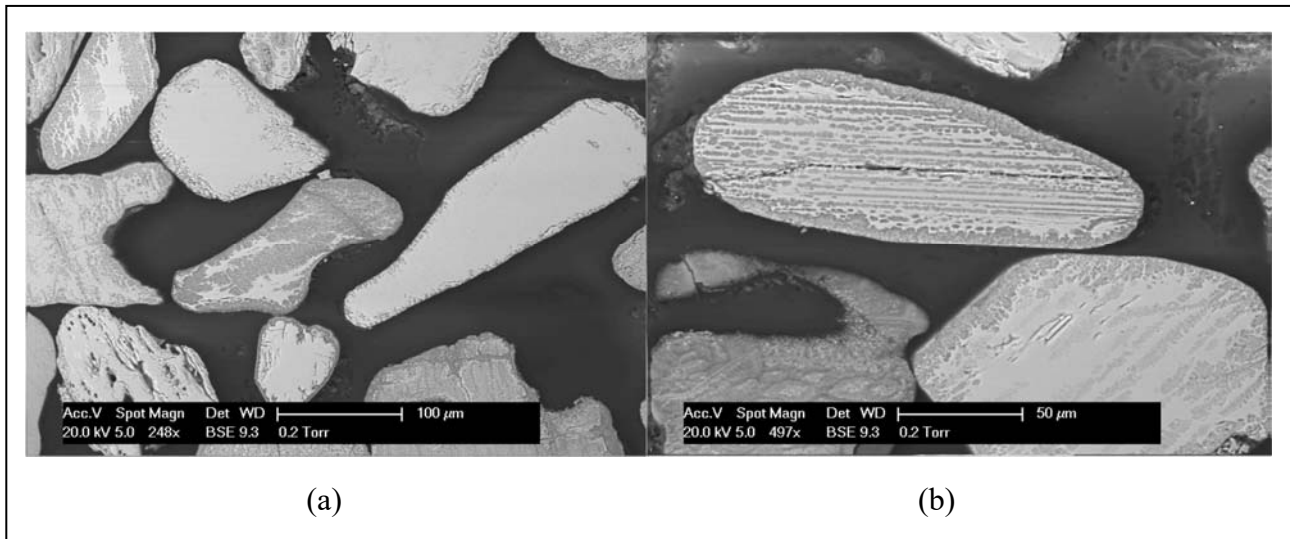


Figure 7: BSE observations after 1 hour leaching duration.

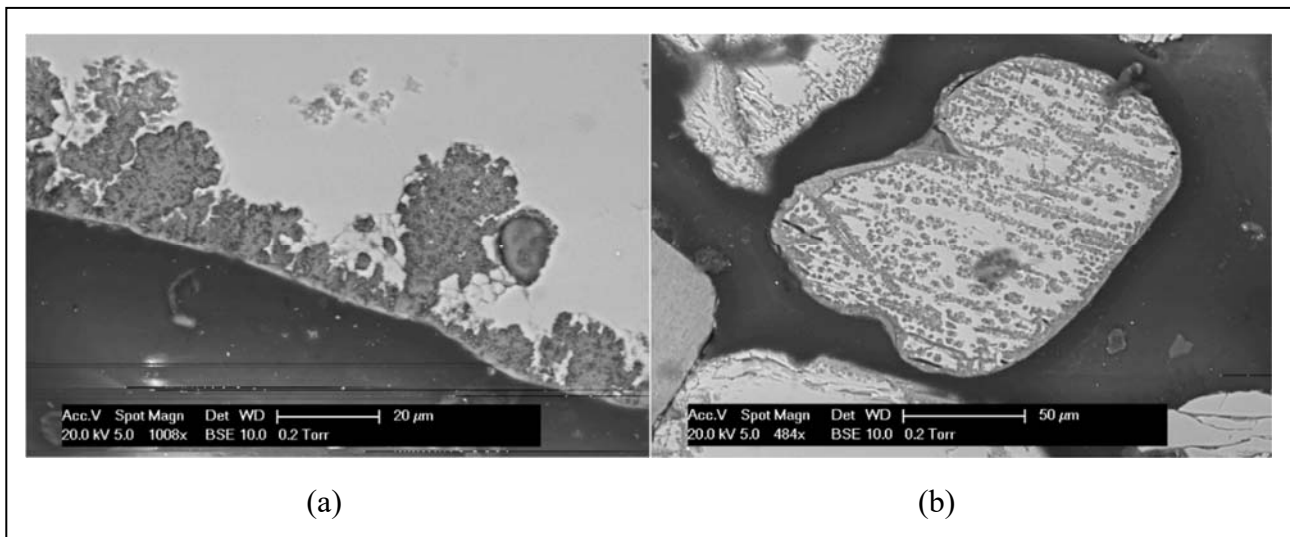


Figure 8: BSE observations after 4 hour leaching duration.

A further attempt was made to validate these observations employing the shrinking core model but due to lack of data this was not possible. As seen in Figure 3, only the 75 and 100°C tests secured titanium precipitation point.

5 Conclusion

The test work being realised has indicated that temperature was the main parameter influencing the level of purification of the synthetic rutile obtained. The pulp density was found to influence the amount of titanium and iron released in the leachate solution. The highest purity achieved was 77 % within process conditions of 100 °C, 15 wt.-% and 360 rpm, failing to reach the targeted purity of 95 %.



SEM analysis showed that temperature and pulp density were intrinsically linked towards contributing to formation of a product layer around the ilmenite grains during the HCl treatment. Despite being effectively observed through SEM, this and other available data could not be conclusively used to validate a suitable kinetic model for the HCl treatment. The data did however show that the HCl purification of the synthetic rutile occurred in two phases. In the first phase, governed by chemical reactions, the acid permeates through the particles facilitated by porosity and grain fractures and dissolves both iron and titanium. When a certain amount of titanium accumulates in the leachate solution, it precipitates and forms a layer around the grains. From this point on, a second phase begins where kinetics are governed by diffusion of iron through the formed layer which prevents further penetration of acid into the grains.

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